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Dichotomous Sampler
A Practical Approach to Aerosol Fractionation and Collection

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DICHOTOMOUS SAMPLER - A PRACTICAL APPROACH TO AEROSOL FRACTIONATION AND COLLECTION

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ABSTRACT

Procedures to size fractionate, collect, and analyze ambient concentrations of particulate matter are described. Emphasis is placed on the design and characteristics of the single-stage dichotomous sampler. A new inlet is described that samples aerosol independent of wind speed and direction, and a discussion of the advantages of a new pneumatic flow control system is included. Comparative results of the high-volume and dichotomous sampler are presented.

This report covers a period from January, 1975 to January, 1978, and work was completed as of January, 1978.

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The authors are indebted to Dr. B. W. Loo of Lawrence Berkeley Laboratory for providing the design shown in Figure 1, and to Dr. Andrew McFarland of Texas A & M University for providing the data and drawings shown in Figures 2 and 3. Also the authors acknowledge the assistance of Dr. George Russwurm and Dr. Dwight Rickle of Northrop Services, Inc. for providing the chemical analyses cited in this report. In addition, we thank the West Virginia Air Pollution Control Board for operating the dichotomous sampler from which some of the data in this report were derived. We acknowledge Dr. S. Freeman and Joseph Nader of System Science, Inc., Chapel Hill, North Carolina for assistance in preparation of Figures 11, 12, 13, and 14 and interpretation of data related to measurements made in St. Louis, Missouri.

SECTION 1

INTRODUCTION

In 1972 the U.S. Environmental Protection Agency launched a program to develop reliable procedures to separate and collect aerosols in two size fractions (<3.5 and >3.5 micrometers (μm) aerodynamic mean diameter). The size fractionation system was designed to collect the aerosols on inert surfaces so that the mass and chemical composition could be measured with a minimum of artifact formation.

Manual (1,2,3) and automated virtual (4,5) dichotomous samplers were developed and for the past 4 years have undergone extensive field testing and wind tunnel studies to characterize their aerosol sampling characteristics. Presently, these samplers are being used in 10 separate field studies across the United States to obtain mass, sulfate, and elemental composition data; these data are being compared with aerosol data collected with the high-volume sampler. The results of these field and wind tunnel tests, as well as the advantages of the dichotomous sampler for characterizing the aerosol content of the atmosphere, are discussed.

SECTION 2

DISCUSSION

VIRTUAL IMPACTION PRINCIPLE

Impactors that separate aerosol particles depend upon the relative balance between inertial and aerodynamic forces. In the conventional aerosol impactor, an airstream turns abruptly as it approaches a flat plate. Particles with the largest inertia tend to maintain a straight trajectory and impact on the plate while the viscous drag forces of the gasflow carry the smaller particles along airflow streamlines. The particles collected on the plate would ideally consist of all sizes above a well defined cut-off diameter. To make a conventional impactor a quantitative particle collector, the impaction surface is coated with a layer of grease to minimize particle bounce errors (6,7). Unfortunately, the grease can interfere with some of the required chemical analyses. Also, the grease may become completely covered with particles and thus reduce the effectiveness of the impactor as a quantitative collector.

In the virtual impaction collection method, instead of having the larger particles collect on grease-coated plates, they are impacted into a slowly pumped void and collected on a filter. Since a small constant fraction of the total flow is being pulled through the void, the portion of fine particles contained in the large particle fraction is directly related to the ratio of the inlet flow and the flow rate in the large particle collector. Figure 1 shows a cross-sectional view of a virtual impactor recently designed by Loo (private communication, B. W. Loo, 1978). It operates at an inlet flow rate of 17 liters/minute and has a 50 percent cut point at 3.5 μm. The shapes and sizes of the orifices were chosen to minimize aerosol losses. Measurements by Loo have shown that the losses are essentially zero in the 1 to 2.5 and 4.5 to

20 μm ranges, and the loss curve peaks at 5 percent for particles in the vicinity of 3.5 μm. Such low losses were measured for liquid particles and represent the worst case. For solid particles, which have a tendency to bounce, the wall losses are even lower (5).

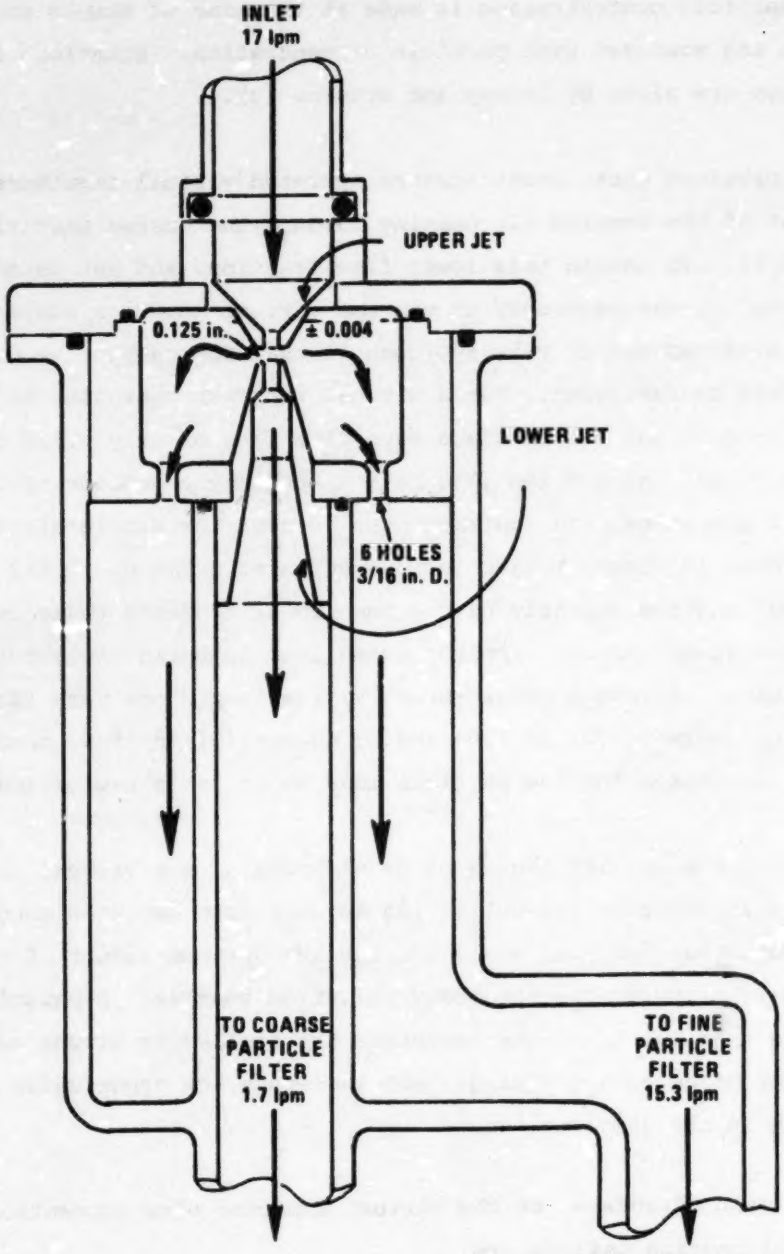


Figure 1. Cross-sectional view of virtual impactor.

For the virtual impactor shown in Figure 1, 10 percent of the sampled air passes through the coarse particle filter. Thus 10 percent of the fine particle mass is collected on the coarse particle filter. A correction of the coarse particle concentration is made at the time of sample analysis and is based on the measured fine particle concentration. Equations for making this correction are given by Dzubay and Stevens (3).

In previous work, investigators operated virtual impactors with only 2 to 5 percent of the sampled air passing through the coarse particle filter (1,2,3,4,5). To obtain this lower flow fraction, and yet maintain adequately low losses, it was necessary to use two virtual impactor stages in series. An obvious disadvantage of this approach is that the sampler is more expensive and complicated to fabricate. For a virtual impactor operating at 14 liters/minute, the two jets of the second stage have diameters of only 0.173 cm (0.068 in) and 0.234 cm (0.092 in) and the jets have a tendency to become clogged after a few months of operation. In contrast, the jets of the single-stage virtual impactor shown in Figure 1 have jet diameters of 0.386 cm (0.152 in) and 0.518 cm (0.204 in) and consequently have a much lower tendency to become clogged. Thus the single-stage virtual impactor costs less to build and provides more reliable results. Although single-stage virtual impactors were first described by Houman and Sherwood (8) in 1965 and by Conner (9) in 1966, these early devices were not optimized for low particle loss as is Loo's new device (Figure 1).

During the initial phases of development of the virtual impactor, it was decided that dividing and collecting aerosol into two size ranges (hence the name dichotomous sampler) would provide the optimum amount of information to distinguish primary from secondary pollution sources. Separating the particles into more than two fractions increases the complexity of the sampler, reduces the amount of aerosol per stage, and increases the opportunity for losses of particles in the sampling train.

The main advantages of the virtual impactor over conventional aerosol size-fractionation designs are:

- Particle bounce and reetrainment problems associated with ungreased impactors and the chemical interferences caused by the required grease coating are eliminated.
- Sufficient quantities of aerosol particles are collected on inert surfaces, providing ideal samples for gravimetric, elemental, and chemical analysis.
- Aerosols are uniformly deposited on filters, providing ideal samples for X-ray fluorescence (XRF) elemental analyses and β-gauge mass measurements.

COLLECTION SURFACES

High-porosity Teflon with 1-μm pores is the most suitable filter medium for use in dichotomous samplers. This filter medium is preferred for the followed reasons:

- Collection efficiency for particles above 0.01 μm greater than 99 percent (10).
- Extremely stable mass for high gravimetric accuracy.
- Negligible tendency to absorb or react with gases.
- Minimal impurities to interfere with analyses for chemical and elemental species.
- Low mass per unit area (desirable for gravimetric, XRF, and β-gauge measurements).

In addition, Teflon filters are ideal for the collection of sulfuric acid since there is little if any interaction with the filter medium. In laboratory experiments, 1 to 100 micrograms (μg) of 0.3-μm droplets of sulfuric acid were deposited on Teflon filters, and > 90 percent of the sulfate and equivalent acidity were recovered.

For gravimetric determination of collected aerosol mass, Teflon collection surfaces are significantly less affected by changes in relative humidity than glass fiber, quartz, and cellulose ester collection surfaces.

For aerosol sampling, the Teflon filters must be supported or mounted in a manner to provide adequate structural strength. In previous studies, we used 37-μm-diameter Fluoropore (Millipore Corporation) filters, which consist of a Teflon membrane bonded to a polyethylene net for support. However, this type of filter tends to curl badly after sampling. Recently, a Teflon membrane filter supported by a thin annular polyester ring became available from Ghia Corporation, Pleasonton, California; this filter has superior handling characteristics. Because the filter is not partly obstructed by a support net, it has improved flow and loading properties. The lower mass per unit area enables better detection limits to be achieved for elemental analysis by XRF.

Investigations are in progress on the collection properties of a newly developed high porosity (>70 percent) Teflon filter with pores in the 2 to 5 μm range. Such filters have much lower flow resistance and should therefore be capable of withstanding longer sampling periods and achieving high particulate loadings without the problem of clogging.

INLET DESIGN

Conventional aerosol samplers have a variety of aerosol intake designs, ranging from the gabled roof used in the high-volume sampler to circular "hat" designs. In these conventional designs, the intake sampling efficiency varies with wind speed and direction. Davies (11,12) has investigated the effects that particle inertia and gravitational settling have upon the performance of aerosol inlets and found that quantitative sampling becomes increasingly more difficult to achieve as the particle size increases above 10 to 20 μm. Our inlet was, therefore, designed to reject particles above 20 μm. Although the high-volume sampler does collect particles larger than 20 μm, the efficiency for collecting such particles depends upon the wind speed and wind direction relative to the orientation of the gabled roof of the sampler.

Under EPA Grant 804190, Andrew McFarland at Texas A & M University has developed an inlet, shown in Figure 2, that is compatible with the dichotomous sampler. McFarland has shown through wind tunnel tests that the particle

sampling efficiency of this inlet remains relatively constant at wind speeds between 4 and 8 kilometers per hour (km/hr). Figure 3 shows inlet particle penetration as a function of particle size at a wind speed of 4 km/hr. Wind tunnel tests are continuing at Texas A & M to further characterize the aerosol sampling efficiency of this new inlet.

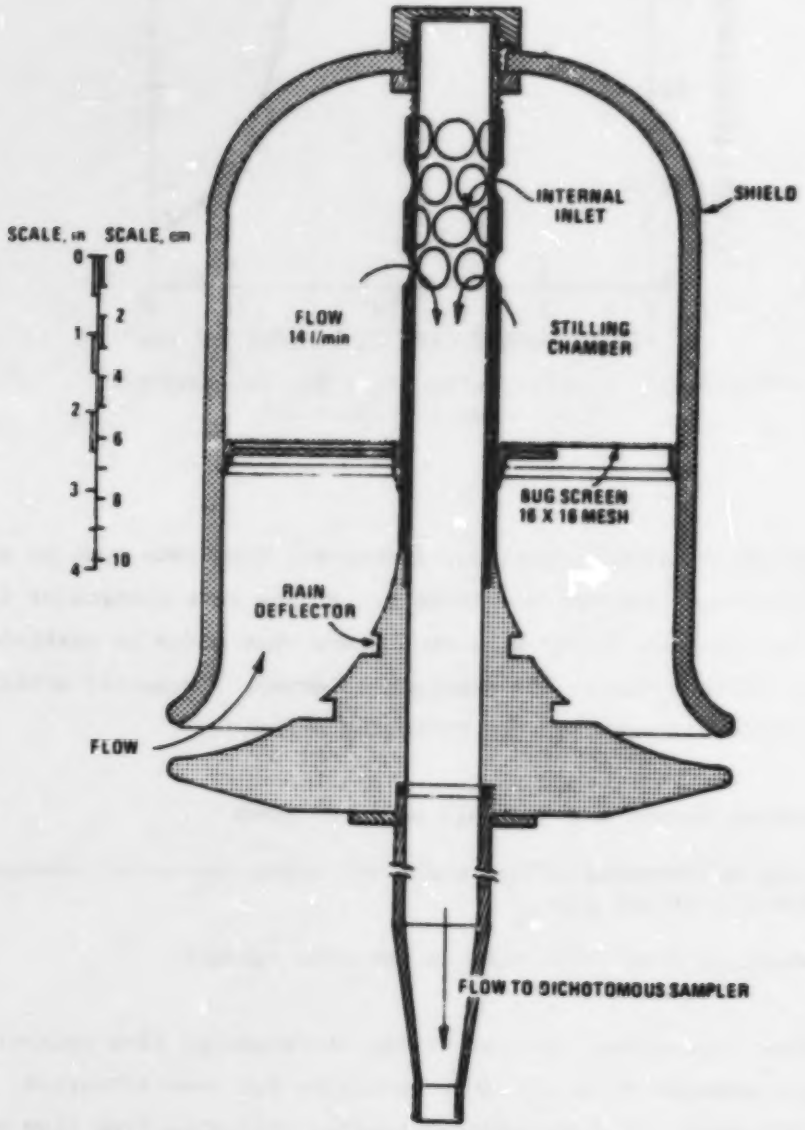


Figure 2. Aerosol inlet for dichotomous sampler.

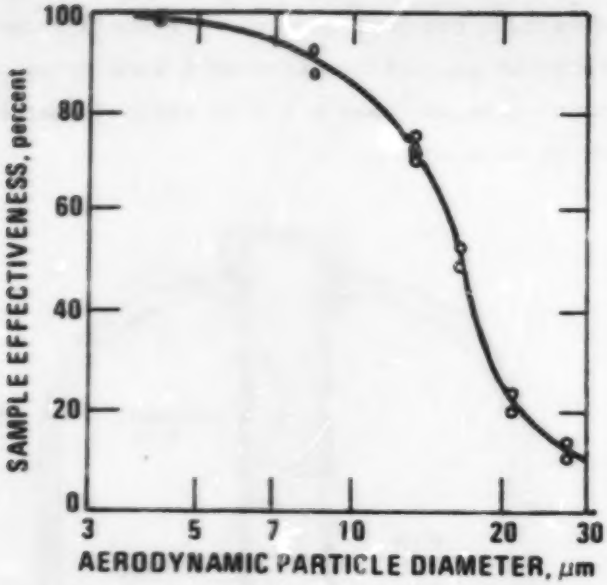


Figure 3. Sampling efficiency for the aerosol inlet shown in Figure 2.

FLOW CONTROL

For quantitative aerosol sampling, a constant flow rate must be maintained through the dichotomous sampler and filters. A flow rate controller is required to compensate for changes in the flow resistance that occur as particles accumulate on the filters during the sampling interval. Presently available flow rate controllers operate on the following principles:

- Anemometer sensor and variable power to pump.
- Pressure differential flow sensor and motor-controlled needle valve between filter and pump.
- Differential flow controller on the pump exhaust.

Of the above approaches, the use of the differential flow controller on the pump exhaust appears to be the most promising for cost effective, routine field use. A schematic of a dichotomous sampler with this type flow control system is shown in Figure 4. A differential pressure regulator in the exhaust line from the pump maintains a constant pressure differential across a fixed orifice and thereby assures a constant flow rate through the system. Because

only a few inexpensive but highly reliable components are needed, this approach provides the ruggedness, reliability, and low cost needed for an aerosol sampler designed for routine field use. McFarland tested the differential flow control system at temperatures from -20 to +40°C, and less than a 5 percent change in flow was observed at a flow rate of 14 liters/minute. Side-by-side comparisons of the differential flow control system with a commercial anemometer flow controller incorporated into two identical dichotomous samplers were performed at Research Triangle Park, North Carolina. Both controllers maintained constant flow to better than 5 percent for pressure drops across the filter of up to 25 cm Hg.

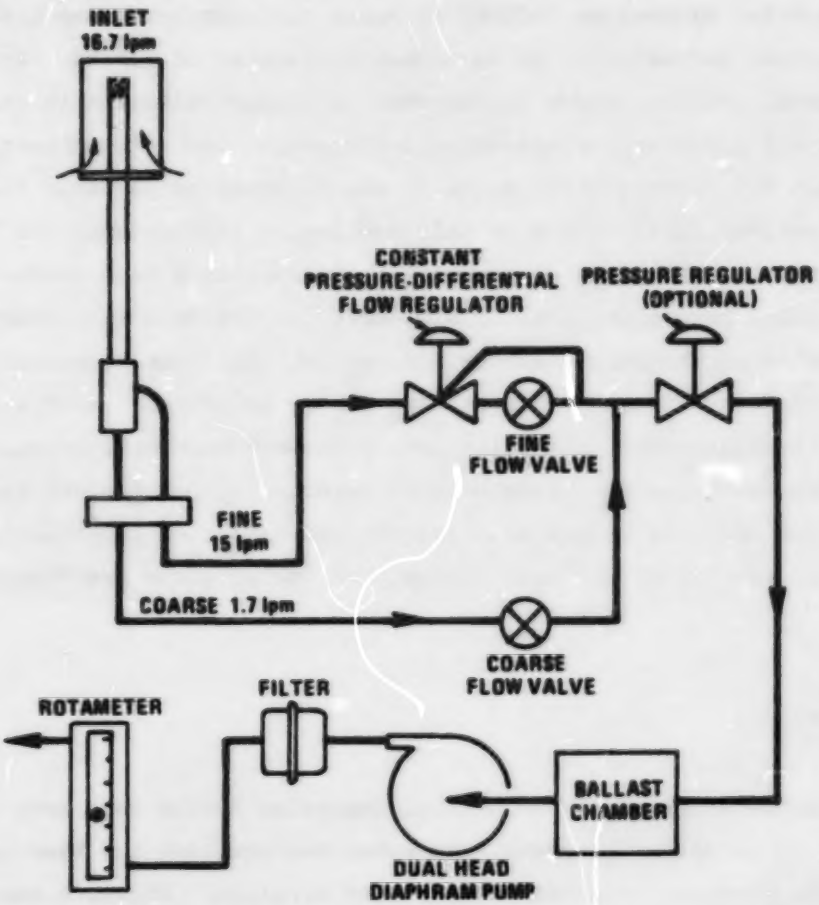


Figure 4. Schematic view of dichotomous sampler with constant flow rate system which uses a pressure regulator to maintain a constant pressure differential across a fixed orifice.

STACKED FILTER SAMPLER

Stevens and Dzubay (1) have previously described an alternative type of dichotomous aerosol fractionating sampler that consists of two filters in series. The first is a Nuclepore filter with 12-μm pore diameters, and the second is a Teflon filter with 1-μm pores. The 12-μm Nuclepore filter has been characterized by Parker et al. (13) to show that when operated at the appropriate flow rate, the collection efficiency curve for particulates with a specific gravity of 2 approximates the Atmospheric Conference of Governmental Industrial Hygienists (ACGIH) criteria for respirable sampling (14) and has a 50 percent cut point at an aerodynamic diameter of 3.5 μm. As the specific gravity varies, there is, however, a slight variation in the collection efficiency curve versus aerodynamic diameter. Tests in ambient air indicate that the fractionation curve is not affected by particle loading (13). One serious difficulty with this sampler is the tendency for particle bounce errors. Recent tests conducted in our laboratory have shown that liquid particles have significantly different collection efficiencies than solid particles of the same diameter. By adding additional chemically treated stages, as shown in Figure 5, H_2S and SO_2 can be collected. Such a sampler is capable of simultaneously collecting both gases and particles to enable determination of the relationship between gaseous and particulate sulfur (15). Because of the particle bounce problem, the gas measuring capability of the tandem filter sampler may be more useful than the particle fractionating capability.

TYPICAL RESULTS

Dichotomous samplers of the virtual impaction design have been operated in a number of geographical areas, and extensive sampling has been conducted in St. Louis, Missouri, and Charleston, West Virginia. Figure 6 shows a comparison of the total (fine plus coarse) mass concentrations determined from high-volume and dichotomous samplers operated in St. Louis during the summer of 1975. In the determination of the mass values, the Fluoropore filters used in the dichotomous samplers were weighed to a precision of 10 μg with an electrobalance in a room adjusted to 40 percent relative humidity. Immediately

before the filters were weighed, they were passed in front of a ^{210}Po radioactive source to remove any electrostatic charge. The glass fiber filters used in the high-volume samplers were weighed with a mechanical balance. The results of this study, shown in Figure 6, indicate the potential of the dichotomous sampler to be used as a substitute for the high-volume sampler for determining mass concentrations. However, in dusty locations when turbulent winds suspend significant amounts of particles larger than 20 μm in the atmosphere, such good agreement between samplers is not expected since the high-volume sampler collects significantly more of the larger particles.

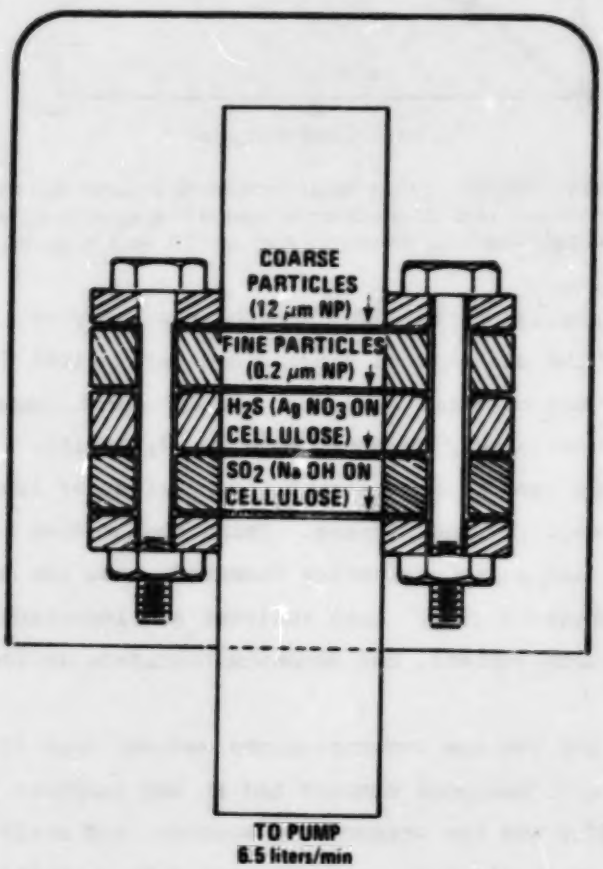


Figure 5. Schematic view of stacked filter aerosol and gas sampler.

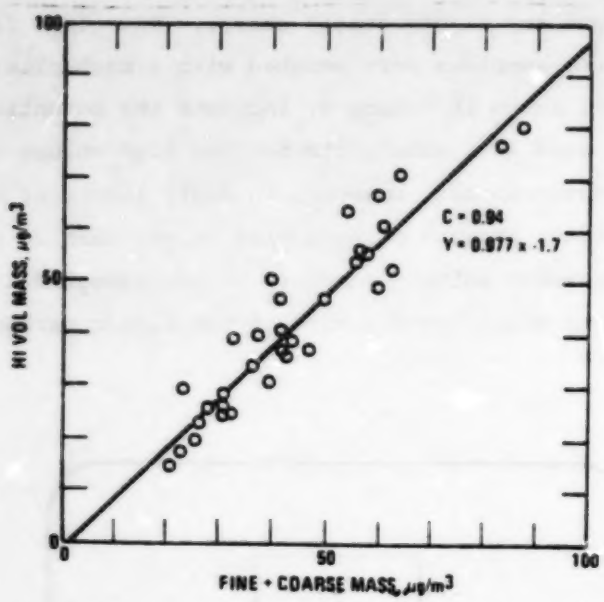


Figure 6. A comparison of total mass concentrations determined using high-volume and dichotomous samplers operated at the St. Louis Botanical Gardens between August 18 and September 7, 1975.

In addition to being suitable for gravimetric analyses, the Teflon collection surfaces of the dichotomous sampler are well suited for making nondestructive elemental and chemical analyses. An XRF spectrometer is used to determine elements with atomic numbers above 13 (2,3,4,16). The Dionex Ion Chromatograph (17) is used to determine a wide variety of ionic species, including sulfate, sulfite, and nitrate. Using the Brosset thorin titration, the Gran titration, and an ion selective electrode, one can determine $SO_4^=$, H^+, and NH_4^+ concentrations (18). Such analyses are important in determining sulfuric acid, ammonium sulfate, and ammonium bisulfate in the sample.

Table 1 shows the average concentrations deduced from 20 sampling periods in St. Louis using a dichotomous sampler and an XRF analyzer. In the fine particle range, sulfur was the predominant species, and analysis of the samples using ESCA (photoelectron spectroscopy) (19) revealed the sulfur to be in the form of sulfate. The paucity of metals in the sample, especially at the rural site, indicates that metal sulfate compounds are of minor importance. The measurements of ammonium and hydrogen ions indicate that the sulfate is usually in the form of ammonium sulfate.

TABLE 1. MASS AND PERCENTAGE COMPOSITION OF SIZE-FRACTIONATED ST. LOUIS AEROSOL SAMPLES FROM AUGUST 18 TO SEPTEMBER 7, 1975

	Urban[a]		Rural[b]	
	Fine, % 29 $\mu g/m^3$	Coarse, % 22 $\mu g/m^3$	Fine, % 26 $\mu g/m^3$	Coarse, % 15 $\mu g/m^3$
Si	1.00	8.00	0.50	4.00
S	12.50	1.40	12.60	0.90
K	0.40	1.20	0.30	0.90
Ca	0.70	8.20	0.50	4.20
Ti	1.10	2.00	<0.10	0.20
Fe	1.40	4.80	0.30	1.30
Zn	0.35	0.20	0.13	0.15
Br	0.33	0.16	0.06	0.04
Pb	2.20	0.60	0.51	0.11

[a] Located at the Missouri Botanical Garden in St. Louis.
[b] Located in an agricultural area in Illinois, 40 km south of St. Louis.

Table 1 also shows that the sulfur in St. Louis occurs predominantly in the fine particle fraction. Figures 7 and 8, which are plots of fine and coarse particle sulfur and mass fractions collected in Charleston, West Virginia, also show that the sulfur occurs predominantly in the fine particle fraction. This same pattern has also been observed for samples collected in Los Angeles, Denver, New York, Philadelphia, Milford (Michigan), and Durham (North Carolina). The only exception to this pattern was observed near a fertilizer plant in East St. Louis, Illinois, where the sulfur in the coarse particle fraction sometimes exceeded that in the fine fraction. A high calcium content in the sample indicated that the particles consisted of calcium sulfate ($CaSO_4$); this was confirmed by microscopic examination.

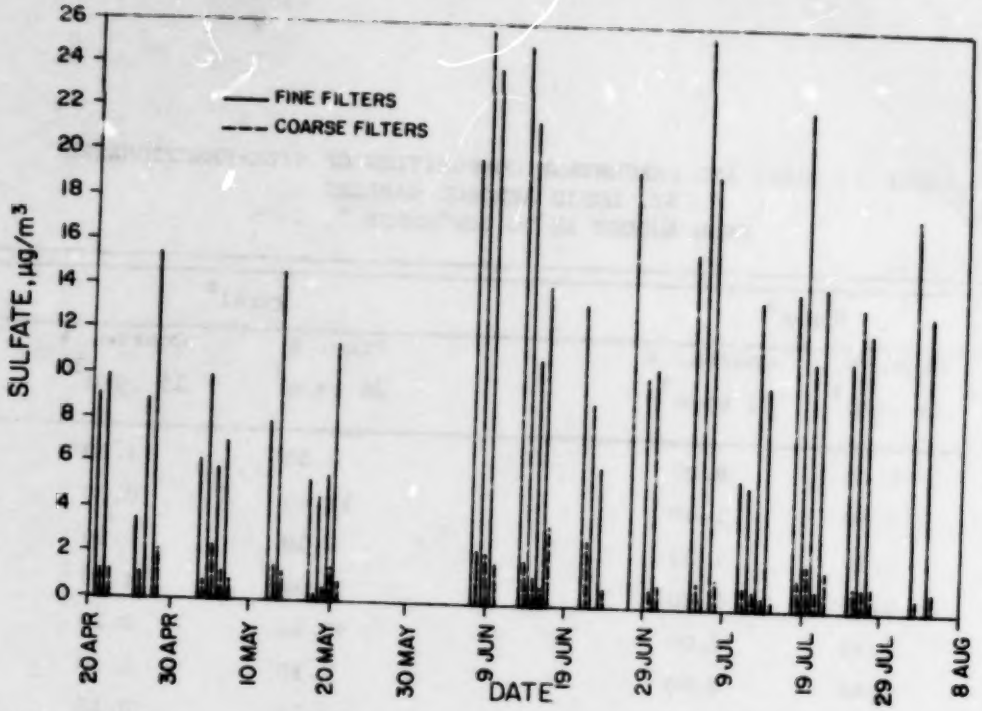


Figure 7. Fine and coarse particle sulfur measurements for aerosols collected in Charleston, West Va., during 1976 using a dichotomous sampler.

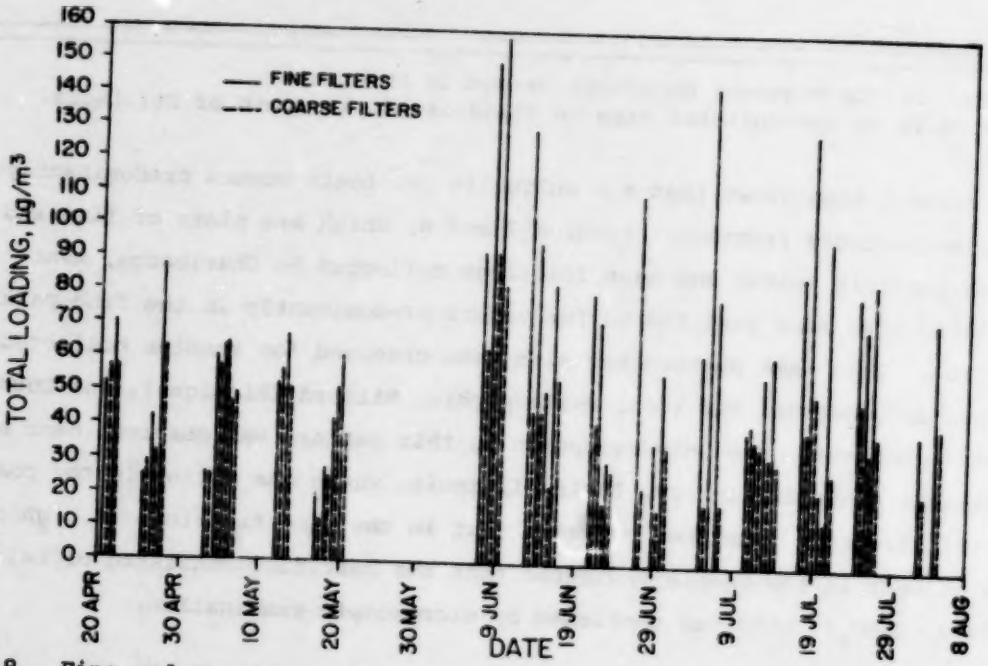


Figure 8. Fine and coarse particle mass measurements for aerosols during 1976.

Figures 9 and 10 show a comparison between XRF measurements for sulfur (expressed as sulfate) and measurements for sulfate on the same set of fine particles collected in Charleston, West Virginia using the ion chromatograph and the thorin titration. The solid lines illustrate the case of perfect agreement, and the dashed line represents the results of linear regression analyses. The closeness of the two lines in Figures 9 and 10 illustrates the excellent agreement between methods. For example, in Figure 9 the expression describing the linear regression is $y = 0.983\ x - 323.1$ with a goodness of fit value of $R^2 = 0.962$. The corresponding expression for Figure 10 is $y = 0.980\ x + 220.6$ and $R^2 = 0.978$. This comparison of the sulfur concentration by XRF with sulfate measurements by ion chromatography strongly suggests that 85 percent or more of the sulfur in particles less than 3.5 μm in aerodynamic diameter is in the form of sulfate. Since the ammonia concentration in the same samples was also found to be present in the same equivalent concentrations as the sulfate, the sulfate is concluded to be in the form of ammonium sulfate. The chemical form of sulfur in the fine particle fraction in Charleston, West Virginia, appears (see above) to be the same as that observed in aerosols collected and analyzed in St. Louis, Missouri.

Ten automated dichotomous samplers (ADS) located in the St. Louis, Missouri, area and part of EPA's Regional Air Monitoring System (RAMS) (20) have been in continuous operation since March of 1974. At these same sites from March 1975 to March 1977, high-volume samplers were operated approximately every third day. The fine and coarse fraction of aerosols collected with the ADS were analyzed for mass and elemental composition (by XRF), and aerosols collected with the high-volume samplers were analyzed for mass and sulfate content (methyl-thymol blue method for sulfate).

Figure 11 presents time series plots for September through December 1975 for two RAMS stations, 106 (located in Busch Botanical Gardens) and 122 (located 45 km North of 106), of total sulfate concentrations determined for aerosols collected by the high-volume and dichotomous samplers. Although dichotomous sampler data are available on a daily basis, only those points are plotted which correspond to days when high-volume data were taken. The data are typical of those obtained in St. Louis during this period.

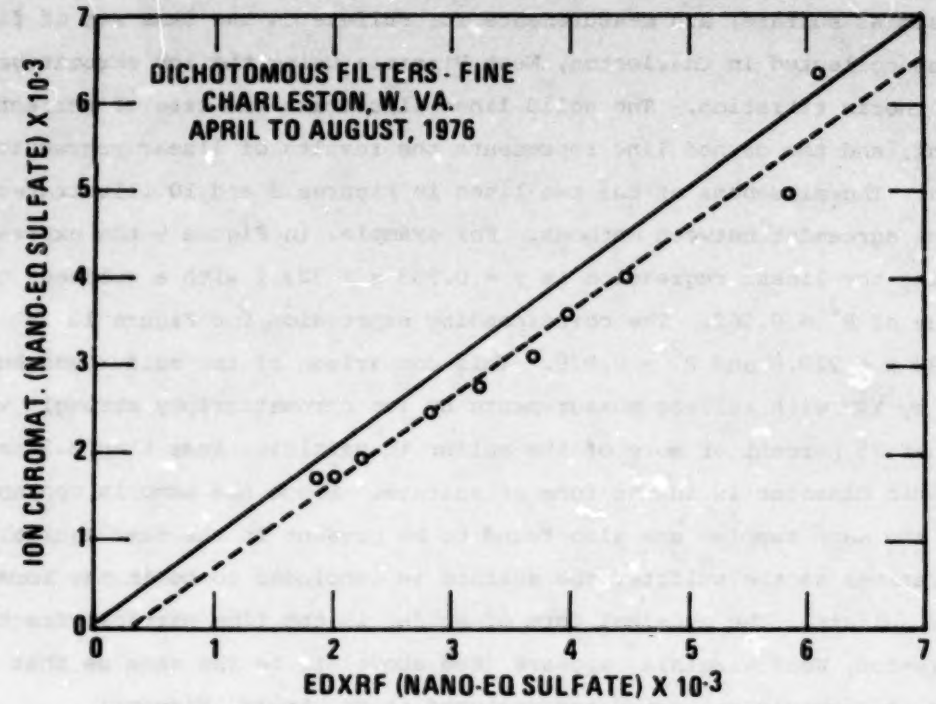


Figure 9. A comparison of fine particle sulfur analyses using an ion exchange liquid chromatograph for sulfate and an XRF spectrometer.

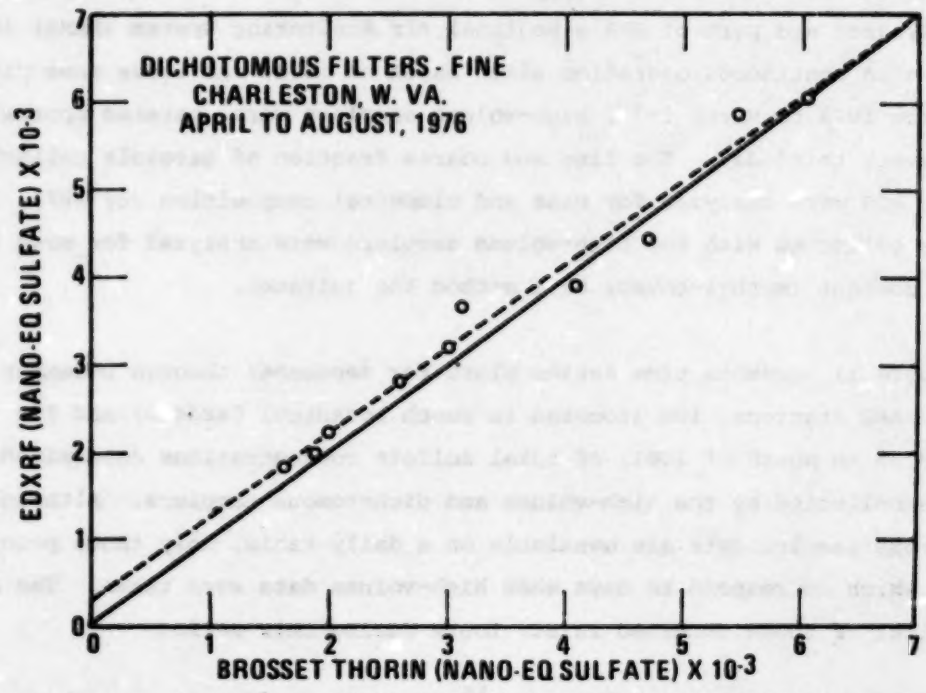
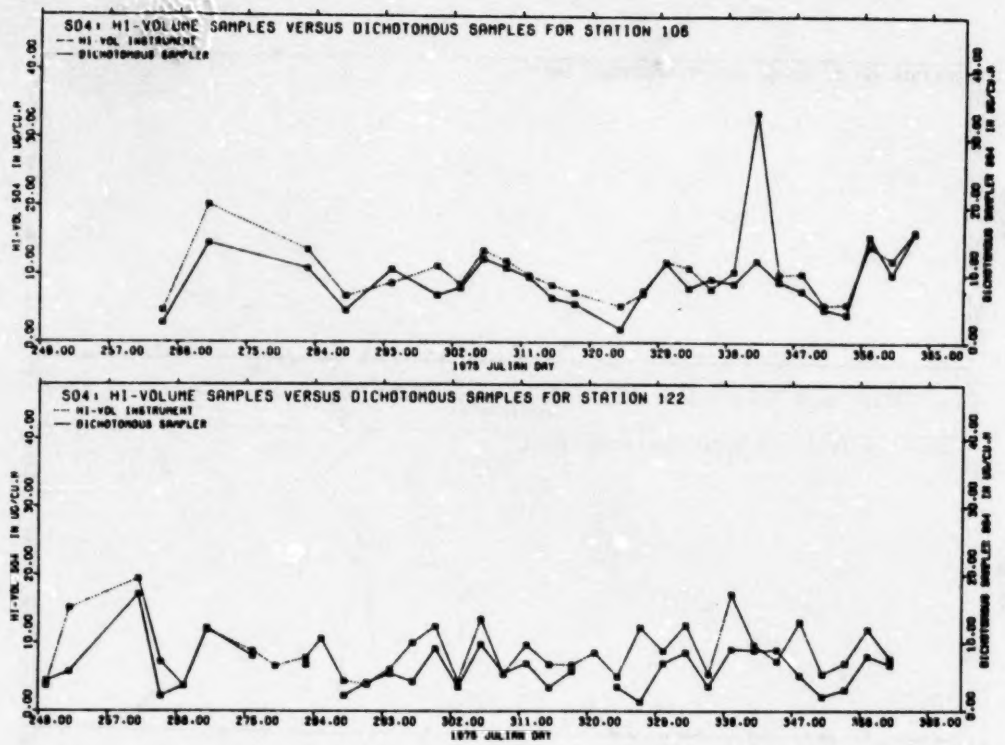


Figure 10. A comparison of fine particle sulfur analyses using XRF and thorin titration methods.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--- HI VOL INSTRUMENT
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SO4: HI-VOLUME SAMPLES VERSUS DICHOTOMOUS SAMPLES FOR STATION 122
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— DICHOTOMOUS SAMPLER
HI-VOL SO4 IN UG/CU.M
DICHOTOMOUS SAMPLER SO4 IN UG/CU.M
1975 JULIAN DAY

Figure 11. Comparison of total sulfate concentrations measured by high-volume and dichotomous samplers at two St. Louis sites.

Inspection of the plots reveals three salient qualitative features of the data:

- The high-volume sulfate data are characterized by spikes in concentration that are local and show no apparent correspondence from station to station.

- The high-volume sulfate concentrations are on the average higher than those obtained with the dichotomous sampler. Preliminary analysis indicates that this conclusion still holds even if outliers during spike periods are not included. This observation is made more apparent by inspection of Figure 12 in which plots for the ratios of high-volume sulfate to total dichotomous sulfate are presented for the same two stations. The average ratio, 1.25, at station 106 is lower than that of 1.44 obtained at station 122.

- The data at a single station for both methods are fairly well correlated.

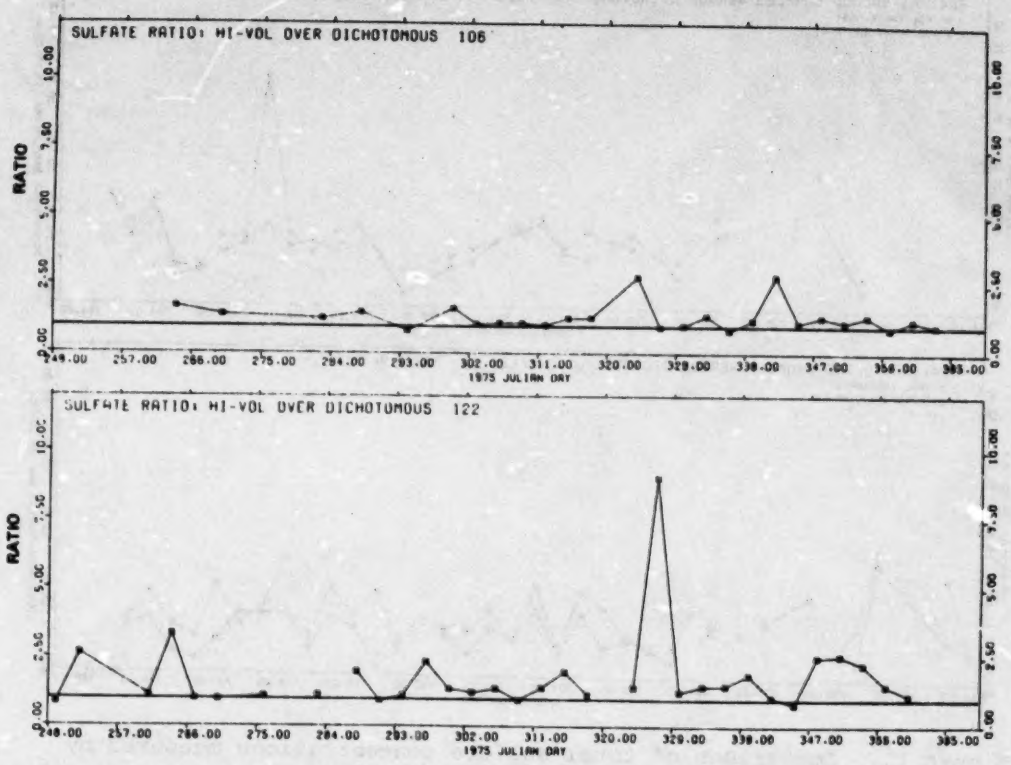

Figure 12. Ratio of high-volume sulfate to total dichotomous sulfate at two St. Louis sites.

Figure 13 shows the dichotomous sampler data in more detail in that simultaneous time series plots for the sulfate found in both fine and coarse fractions are presented. It is clear from these data that in the particle size range below 20 μm the overwhelming proportion of sulfate is contained in the fine fraction (below 3.5 μm).

A brief summary of St. Louis sulfate concentrations is shown in Table 2 for eight RAMS stations monitoring sulfate by both the high-volume and dichotomous sampler methods. For a composite of eight stations the time averaged high-volume sulfate concentration was 10.3 $\mu g/m^3$ while that for the dichotomous sampler (fine plus coarse fractions) was 7.8 $\mu g/m^3$. For every station the time-averaged concentration measured by the high-volume sampler exceeded that measured by the dichotomous sampler. The discrepancy between the two methods ranged from 23 to 53 percent (less if outliers are excluded). Although no firm explanation of this preliminary result is offered, either

aerosol sampling efficiency variations or sulfate artifact formation on the glass fiber filters of the high-volume sampler is suspected. Note that if the measured difference were real, there would be a significant sulfate contribution from particles of greater than 20-μm aerodynamic size. (Such particles might be unimportant insofar as human health hazards are concerned.) The dichotomous sampler data show that on 94 percent of all the days sampled, the percentage of sulfur in the fine fraction (below 3.5 μm) was no less than 70 percent.

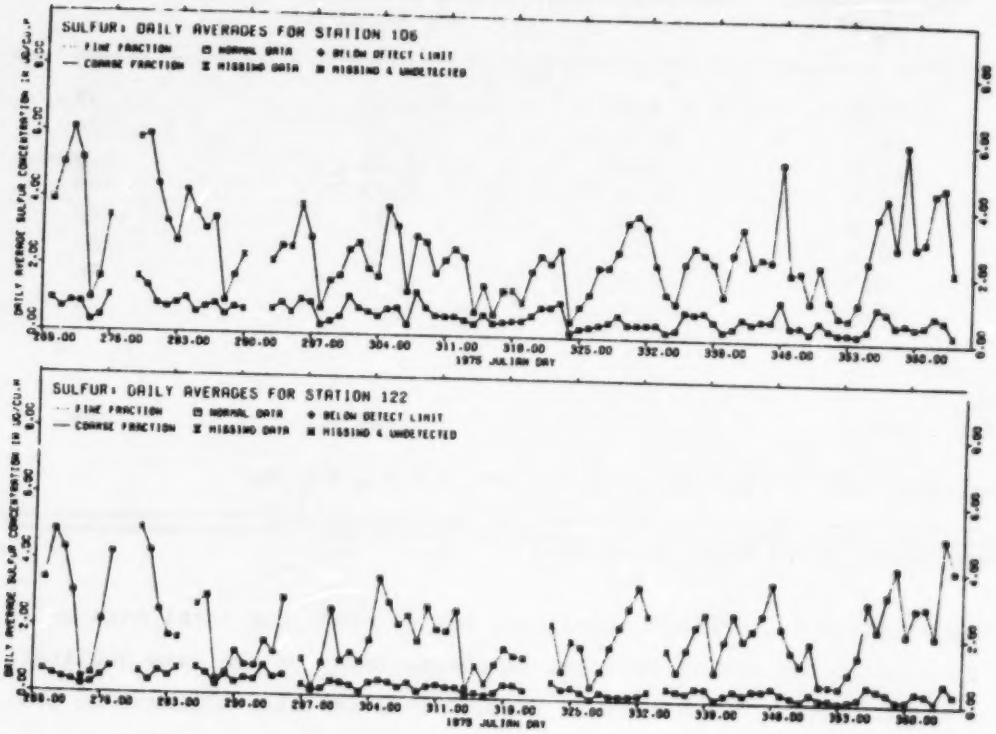

Figure 13. Fine and coarse dichotomous sulfur fractions at two St. Louis sites.

Table 2 also shows that the time-averaged high-volume sampler data correlate well with the dichotomous sampler data. A calculation of the Spearman rank-order correlation coefficient yields a value of 0.83 at a significant level of >0.99 (21).

TABLE 2. SUMMARY OF ST. LOUIS SULFATE CONCENTRATIONS DETERMINED BY TWO METHODS FOR THE PERIOD SEPTEMBER THROUGH DECEMBER 1975

RAMS station number	Average high-volume concentration, $\mu g/m^3$	Average total dichotomous concentration, $\mu g/m^3$	Ratio high-volume concentration to total dichotomous concentration	Percentage of days when fine S/total S>0.70
*106	11.0	8.9	1.25	97
108	12.7	10.0	1.27	79
112	10.6	9.2	1.23	95
115	9.6	7.8	1.23	99
118	9.9	6.6	1.50	83
120	9.9	7.3	1.35	100
*122	8.9	6.2	1.44	94
124	9.8	6.4	1.53	99
Average of the 8 RAMS stations	10.3	7.8	1.32	94

Spearman rank-order correlation coefficient = 0.83, P<0.01

*Stations presented in time series plots

Figure 14 shows (corresponding) time series plots for total mass collected by high-volume and dichotomous samplers. Many of the same qualitative features noted above for the sulfate measurements are also apparent in the mass data: spikes in the high-volume measurement and a higher (in some cases much higher) value obtained by the high-volume sampler. The time-averaged value for the ratio of high-volume mass to total dichotomous mass at station 106 was 1.8. The corresponding ratio at station 122 was 1.2. Recall that the sulfate ratios were higher at station 122 than at station 106. Further work is needed to clarify these relationships for both sulfate and mass.

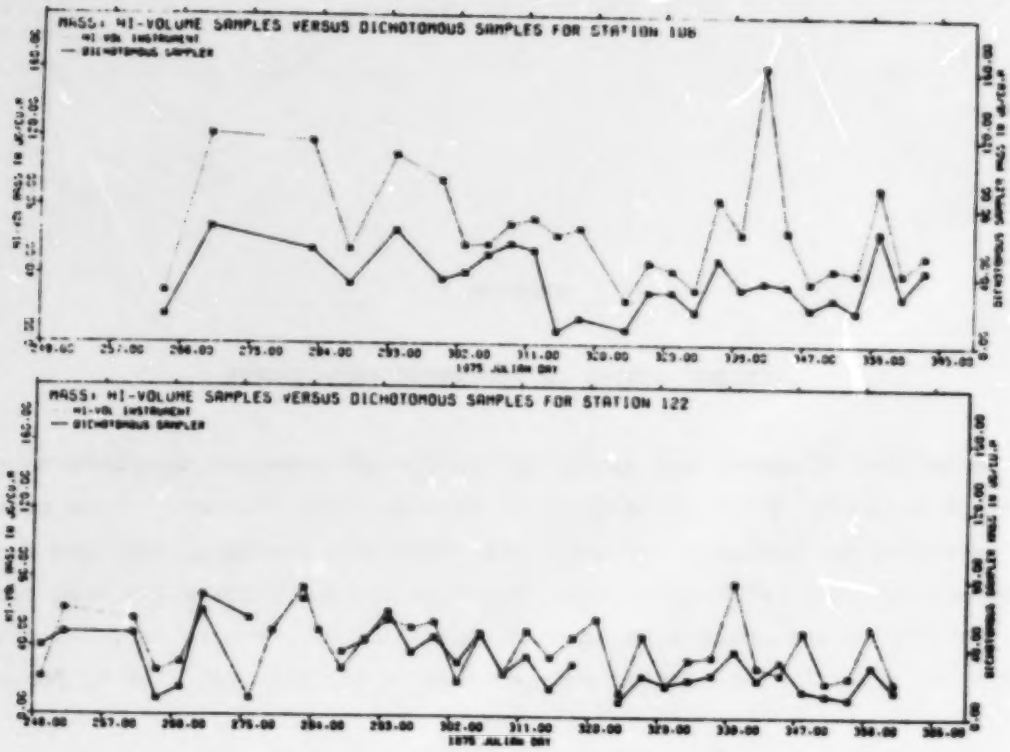
MASS: HI-VOLUME SAMPLES VERSUS DICHOTOMOUS SAMPLES FOR STATION 108
HI-VOL INSTRUMENT
DICHOTOMOUS SAMPLER
MASS: HI-VOLUME SAMPLES VERSUS DICHOTOMOUS SAMPLES FOR STATION 122
HI-VOL INSTRUMENT
DICHOTOMOUS SAMPLER

Figure 14. Comparison of total mass concentrations measured by high-volume and dichotomous samplers at two St. Louis sites.

SECTION 3

CURRENT STATUS OF EQUIPMENT DEVELOPMENT

Prototypes of manual and automated dichotomous samplers have been thoroughly tested to establish their reliability as aerosol fractionators. These prototypes were expensive to fabricate because of the machining precision required and the expensive flow controllers used. The flow control problem has been potentially solved by employing a low-cost differential flow controller, but problems still exist with the fabrication and assembly of the critical flow components.

EPA has recently requested Beckman Instruments, Fullerton, California, to design and fabricate a manual dichotomous sampler available for less than $1,900 and an automated sampler available for less than $4,500. In certain parts where the components are made in two halves, Beckman proposes to use metallized molded plastics that are bonded together with adhesive. Since the concentricity of inlet nozzles and receptor orifices in the impactor stages is critical, each impactor stage is made of one piece. Then the assembly of parts becomes non-critical. Nozzles and receptors remain aligned and are easily removed and replaced as units for varying the cut points and for cleaning. The manual sampler built by Beckman will be designed for direct installation in exposed locations with no additional housing required. The instrument will be housed in a seamless glass-reenforced plastic lay-up. The housing will have an access door for convenient filter changing and virtual impactor cleaning.

In addition to the work of Beckman, Sierra Corporation, Carmel Valley, California, is currently selling a dichotomous sampler developed by Environmental Research Corporation (ERC), St. Paul, Minnesota, under EPA Contract 68-02-1744. Sierra couples the ERC sampler with their flow controller and special inlet system and markets the complete aerosol collection device at about $3,500.

The automated system is similar to the manual sampler. Common components include inlets, virtual impactors, flow controllers and air transport, and external housing. The sampler-changing mechanism will be adapted from the sample-changer mechanism developed for EPA by Lawrence Berkeley Laboratory (4,5). Magazines containing up to 36 pairs of filters will be installed through an easy-access service port. The changing of the filters will proceed according to instructions from the control module. The control module will be composed of a microprocessor and pressure drop sensing element. When the pressure across the filter exceeds a pre-set value, the filters will automatically be changed. In most cases the filters will be changed before the pressure drop exceeds the pre-set level, i.e., once every 24 hours. During periods of air stagnation, particulate levels may exceed several hundred micrograms per cubic meter. In these instances when the filters begin to clog, the filters will be changed before the flow decreases by more than a few percent of the initial setting.

This new family of aerosol samplers is a marked departure from previous approaches of aerosol sampling. Years of prototype testing, evaluation, and intercomparisons have been performed. These tests have culminated in the current design concepts soon to be implemented by several instrument manufacturers and should provide the various air pollution control agencies with a powerful tool to aid in understanding sources and transport of atmospheric aerosols.

REFERENCES

1. Stevens, R.K., and T.G. Dzubay. Recent Development in Air Particulate Monitoring. IEEE Trans. on Nucl. Sci., NS-22:849-855, 1975.

2. Dzubay, T.G., and R.K. Stevens. Ambient Air Analysis with Dichotomous Sampler and X-Ray Fluorescence Spectrometer. Environ. Sci. Technol., 9:633-668, 1975.

3. Dzubay, T.G., and R.K. Stevens. Application of the Dichotomous Sampler to the Characterization of Ambient Aerosols. In: X-Ray Fluorescence Analysis of Environmental Samples, T.G. Dzubay, ed. Ann Arbor Science, Ann Arbor, Michigan, 1977. pp. 95-105.

4. Goulding, F.S., J.M. Jaklevic, and B.W. Loo. Fabrication of Monitoring System for Determining Mass and Composition of Aerosols as a Function of Time. EPA-650/2-75-048, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, 1975.

5. Loo, B.W., J.M. Jaklevic, and F.S. Goulding. Dichotomous Virtual Impactors for Large Scale Monitoring of Airborne Particulate Matter. In: Fine Particles, B.Y.H. Liu, ed. Academic Press, New York, New York, 1976. pp. 311-350.

6. Wesolowski, J.J., W. John, W. Devor, T.A. Cahill, P.J. Feeney, G. Wolfe, and R. Flocchini. Collection Surfaces of Cascade Impactors. In: X-Ray Fluorescence Analysis of Environmental Samples, T.G. Dzubay, ed. Ann Arbor Science, Ann Arbor, Michigan, 1977. pp. 121-131.

7. Dzubay, T.G., L.E. Hines, and R.K. Stevens. Particle Bounce Errors in Cascade Impactors. Atmos. Environ., 10:229-234, 1976.

8. Houman, R.F., and R.J. Sherwood. The Cascade Centripeter: A Device for Determining the Concentration and Size Distribution of Aerosols. Am. Ind. Hyg. Assoc. J., 26:122-131, 1965.

9. Connor, W.D. An Inertial-Type Particle Separator for Collecting Large Samples. J. Air Poll. Con. Assoc., 16:35-38, 1966.

10. Liu, B.Y.H., and G.A. Kuhlmey. Efficiencies of Air Sampling Media. In: X-Ray Fluorescence Analysis of Environmental Samples, T.G. Dzubay, ed. Ann Arbor Science, Ann Arbor, Michigan, 1977. pp. 107-119.

11. Davies, C.N. The Aspiration of Heavy Airborne Particles Into a Point Sink. Royal Soc. London Proc., Ser. A, Vol. 279(1378):413-419, June, 1964.

12. Davies, C.N. The Entry of Aerosols Into Sampling Tubes and Heads. Brit. J. Appl. Phys., Ser. 2, Vol. 1(7):921-932, 1968.

13. Parker, R.D., G.H. Buzzard, T.G. Dzubay, and J.P. Bell. A Two Stage Respirable Aerosol Sampler Using Nuclepore Filters in Series. Atmos. Environ., 11:617-621, 1977.

14. ACGIH. Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1973. American Conference of Governmental Industrial Hygienists, P.O. Box 1937, Cincinnati, Ohio 45201.

15. Lorenzen, J.A. Environmental Monitoring Device for X-Ray Determination of Atmospheric Chlorine, Reactive Sulfur, and Sulfur Dioxide. In: Advances in X-Ray Analysis, Vol. 18, W.L. Pickles, C.S. Barrett, J.B. Newkirk, and C.O. Ruud, eds. Plenum Press, New York, New York, 1975. pp. 568-578.

16. Jaklevic, J.M., F.S. Goulding, B.V. Jarrett, and J.D. Meng. Applications of X-Ray Fluorescence Techniques to Measure Elemental Composition of Particles in the Atmosphere. In: Analytical Methods Applied to Air Pollution Measurement, R.K. Stevens and W.F. Herger, eds. Ann Arbor Science, Ann Arbor, Michigan, 1974. pp. 123-146.

17. Mulik, J., R. Puckett, D. Williams, and E. Sawicki. Ion Chromatographic Analysis of Sulfate and Nitrate in Ambient Aerosols. Analytical Letters, 9:653-663, 1976.

18. Brosset, and M. Fern. Man Made Airborne Acidity and Its Determination. IVL Publications B-314A, Gothenburg, Sweden, 1976.

19. Novakov, T., S. G. Chang, R.L. Dod, H. Rosen. Chemical Characterization of Aerosol Species Produced in Heterogeneous Gas-Particle Reactions. Lawrence Berkeley Laboratory Report No. LBL-5215, Lawrence Berkeley Laboratories, Berkeley, California, 1976.

20. Myers, R.L., and J.A. Reagan. The Regional Air Monitoring System, St. Louis, Missouri. In: Proceedings of the International Conference on Environmental Sensing and Assessment, Las Vegas, Nevada, Sept. 14-19, 1975.

21. Nie, N.H., C.H. Hull, J.G. Jenkins, K. Steinbrenner, and D.H. Bent. Statistical Package for the Social Sciences, McGraw-Hill, New York, New York, 1975.